PROCEEDINGS OF

THE ROYAL SOCIETY.

Section A.—Mathematical and Physical Sciences.

On Electro-Crystalline Properties as Conditioned by Atomic Lattices.

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(Received January 6, 1921.)

The method of analysis of crystal lattices by ultra-optical spectra, introduced and applied by W. L. and W. H. Bragg, has led to the view that the ultimate crystalline element is (or may be) the atom* and not the chemical molecule: so that each atom, presumably with its ionic electric charge, often stands in identically the same relation to a number of surrounding atoms of the other kind with opposite charge, and therefore cannot be associated physically with any one of them. The alternative view, previously perhaps the more natural on the physical as distinct from the tactical side, was to regard the chemical molecule as the crystalline unit: its associated positive and negative atomic ions might then form an electric diad with definite polar moment orientated in definite direction,—and with this the new schemes come into contrast. The following general remarks may be useful towards comparison of these two fundamentally different conceptions. Other reasons will incidentally emerge, besides the results of analysis by X-rays, favouring the view that facts of nature point rather towards the atomic mode of crystal structure.

These considerations deal with fundamental ideas that must be reckoned with, on an ionic view, apart from the detail essential to the science of crystallography. It will however be convenient to fix attention by simple cases; for example, the typical space-lattice for an alkaline halide such as rocksalt NaCl, in which the crystalline unit has been ascertained to be

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* Rather the ion, which may be an atom or a group of atoms. The problem as to how stability of the crystalline structures is assured by interaction of the electric forces with the forces concerned in the packing of the molecules is outside the scope of this note, which is concerned with analysing the results of various types of structure.

for each ion a "face-centred" cube, the corners for one component being the centres of the edges for the other. In the two structural plane diagrams, which represent the atoms projected perpendicular to a diagonal, the letters a may represent the negative atomic ions Cl, and the letters b the positive ones Na. In the second diagram a diagonal boundary face constituted of Cl atoms is succeeded by parallel planes, alternately of Na and Cl, and finally one of Na, these planes of like atoms being obliquely placed: this diagram invites description at sight as that of a very strongly polarised aggregate, each bipolar element being made up of a Cl combined with an adjacent Na below it. On the other hand in the first diagram the boundary face is composed of both kinds of ion in equal numbers: and if the aggregate is regarded as sorted into bipolar elements, each consisting of an atom in one face and the adjacent atom in the next parallel plane, the polarities of the consecutive elements in all directions are equal and opposite, so that the mass appears as unpolarised when the effective element of volume is large enough to include a considerable number of such bipolar elements.

a	b	a	b
b	a	b	a
a	b	a	b
b	a	b	a

a			
b	a		
a	b	a	
b	a	b	a
	b	a	b
		b	a
			b

These two modes of description of the same lattice can of course be only apparently in contradiction. In the Poisson-Kelvin conception of a polarised medium, the polarity can be replaced, except for locally constitutive purposes,* by equivalent distributions of simple density throughout the volume and over the surface. In a crystal, in which the structure is strictly uniform, the volume density is zero on both these modes of polar specification of NaCl: and to reconcile them it is the surface density that must claim attention.

These regular polarities are special, as being far more precise distributions than the fortuitous aggregates of polar molecules that are the foundation of the usual theory of a polarised medium, as constructed by the process of averaging over an element of volume.

By a mathematical device familiar in the elementary analysis of optical diffraction, it is possible to reduce the polarity overtly associated with the second NaCl diagram. We have only to regard each ionic charge as divided into two halves, of which one is associated with half of the next ion in front and the other with half of the next ion in rear along a row, thus forming two adjacent bipolar elements, of opposite signs, and therefore practically cancelling each other except as regards local physical quality of the substance. In this way the electric system is reduced to two surface densities of opposite signs, represented by half the distributions of ions on the opposite boundary planes. The factor one-half at first glance may seem to be a discrepancy between this regular discrete distribution of poles and the Poisson-Kelvin averaged theory of continuous polarisation: the difference may be traced to the circumstance that the polar pairs in the second diagram occupy only half the intervals along a row of atoms, the rest of the length being vacant.

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* Compare for example, 'Æther and Matter,' 1900, p. 252.

The equivalent surface density of ions, here contemplated over limited areas, would involve enormous electric fields in the substance between these intensely electrified boundary planes, such as could not possibly subsist. It must be compensated locally on each element of surface. If conducting quality of metallic type is absent so that free electrons are excluded, this can only be by a distribution of ions of the opposite kind added on outside the surface layer, but only of half the number that would make up a complete stratum of the crystal. We conclude that a boundary plane, in a crystal, such as contains only one kind of ion, must be a ragged surface instead of a smooth one; for it involves the presence of an additional half stratum of the other kind.* When a crystal face grows, the ions must be laid down alternately, and also so that successive pairs constitute opposed polar elements: thus the modes of growth of the two types of face would be different: and the same would apply to modes of dissolution.

The crystalline structure of various metals has been found by W. L. Bragg and other investigators to agree with this specially simple face-centred cubical space-lattice of Na, which in the scheme of NaCl is electrically compensated by the similar but displaced lattice for Cl. In case of the pure metal also, electric compensation must be provided, most naturally perhaps† by locating negative electrons more or less permanently in the positions occupied in the salt by the Cl ions.

Hitherto there is on this view no provision for the liberation of latent surface electric charge by change of temperature or by stress, as is conspicuous in crystals such as tourmaline. For the number of ions or electrons required for a neutralising surface distribution depends only on the number of ions in the crystal, and is not affected by change of its form or dimensions.

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* An oblique artificial face should exhibit similar features as regards electric excitation, unless it were made up of minute facets with boundary planes in the principal directions of the crystal.

† Lindemann ; Born and Landé ; also Borelius, 'Phil. Mag.,' 1920.

This additional feature will be introduced if the positive and negative ions are not equidistant along their lattice rows. Thus for the line of ions represented in the diagram, we have to pair into bipoles by resolving each charge, say the one at B, into unequal fractions, so that the moments formed by their association with fractions of the adjacent charges at A and C may balance. The uncompensated charge at the terminal ion A is now e.AB/AC instead of $\frac{1}{2}e$; and similarly at the other end of the chain.

A B   C D   E F
b a   *b a*   *b a*   ...

These residual charges on the surfaces of the crystal must, as before, be masked by local distribution of additional ions or by electrons. But the masking charge no longer stands in the same simple relation to the number of surface atoms: and whenever, by thermal expansion or by stress, the ratio AB/AC becomes altered in the crystal, the compensation at the surface will become deranged, indications of free surface electrification will appear, and persist until they are wiped out by further accretion of compensating charge. An extremely small change in the ratio AB/AC would suffice to cover the facts of pyro- and piezo-electrification.

When each crystalline element is itself polarised with regard to a definite axis, the Poisson-Kelvin theory of a medium polarised *in bulk* can be formulated. But in the configuration here under review it seems to require modification; the positive and negative elements are independent ions, in regulated positions, and it has been seen that we can regard them as associated in pairs in various ways; so that there is no definite unique specification in terms of polarity per unit volume of the medium. But the analytical theory of the charges set free in crystals by stress or change of temperature seems to have hitherto been developed with regard to an assumed specific electric polarity in the crystal, having reference to some definite axis; with the result that cases were outstanding which would not come under the rules,*

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* It appears that an intrinsic polarity, or regular static collocation of electrons within each molecule, would suffice by interacting with crystalline deformation, to include within the theory the octopolar pyro-electric quality detected long ago in cubic crystals by Haüy: *cf.* Lord Kelvin's 'Baltimore Lectures,' p. 561, or "Æpinus Atomized," 'Phil. Mag.,' 1891.

The formal theory of Voigt ('Krystalloptik,' §§ 128–9) seems to regard only *induced* polarity, which is expressed as a function of deformation *alone*, whether due to stress or to uniform change of temperature, by means of a sufficient number of moduli. It appears from recent experiments by Roentgen, Hayashi, Ackermann, and Lindman, in and had to be referred to internal strain set up by cooling. On the present view such cases perhaps cease to be abnormal; for a direction of polarity cannot be ascribed to the compound lattice. The theory thus opens out into a new form of problem in crystalline tactic; the opposing ions within the crystal have to be paired, either as wholes or in fractions, so that the moments of the adjacent pairs shall everywhere cancel out. Then uncompensated ions on the surface remain over unimpaired, except so far as they are masked by additional electrons or ions brought there from without; they would give rise to the emergence of free surface charge when the physical state of the crystal is changed.

Such release of latent electricity should not appear on surfaces constituted by equal numbers of the two ions. The specification of its distribution, peculiar as being locally conditioned, should of course be definite and unique, by whatever process of pairing it is reached. The electric abnormalities caused by cracks and clefts on a crystal surface would now arise naturally, without requiring local stress due to unequal heating, as had to be suggested.

Dielectric excitation in a uniform electric field would now be represented by the positive and negative component lattices being drawn towards opposite directions by the field, with resulting electric moment depending on their *relative* displacement. For NaCl in a uniform field of electric force the two similar lattices of the Na atoms and the Cl atoms are thus displaced relative to each other without deformation of either though with very slight change of structure; and this applies generally, for all component lattices are similar. Here also the electric displacement could be fixed and compensated, by local surface charge masking the polarisation—for example by sweeping a flame over the surfaces while the inducing electric field is in action. In the alternating electric fields of radiation it is, on final analysis, this oscillatory motion relative to each other* of the component ionic lattices that influences the speed and mode of propagation of the waves.

If the crystal has not sufficient symmetry (in fact, in the lattices that have spiral features) this relative displacement of the two ionic groups in the element of volume, by an applied electric field, may be one of twisting type, involving a rotational part to which is to be ascribed the chiral structural

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which special precautions were taken as to uniformity of temperature, that these moduli are not much, if at all, affected by temperature (*cf.* Voigt, 'Ann. der Physik,' 1915); as would be natural on the present order of ideas. It was in fact held by J. and P. Curie, the discoverers of piezo-electricity, that pyro-electricity is to be regarded as a result of deformation alone and not as essentially thermal.

* Only partially regular and elastic in the case of metals: the super-conductance of K. Onnes has been ascribed (Lindemann) to complete regularity owing to thermal agitations being suppressed.

rotation of plane of polarisation of light transmitted through the crystal. There are thus the two modes of origin of this chiral optical rotation. One depends on crystalline structure alone, and disappears on fusion of the crystal. In the other the molecule itself, usually a complex aggregate of atoms, undergoes in an electric field this spiral relative deformation of its ionic constituent groups, involving screw quality; and to this exent the optical chirality will remain on fusion or solution, but in altered amount, usually much smaller, as was observed in the case of sucrose by Pocklington. From achiral molecules a crystalline structure of chiral quality can thus be formed. As chiral molecular quality is not of vector type, it could not be annulled by fortuitous orientations as in a fluid, when molecules of opposed chiralities are not present. If the chirality of the molecules is isotropic (*cf.* Lord Kelvin's isotropic helicoid) there would not be much alteration by fusion of that small intrinsic part of the chirality in bulk; if uniaxial, the maximum would be reduced to about one-third.

Double refraction, limited in form* in accord with the dynamical equations of MacCullagh and of Maxwell, will arise from any kind of deviation from cubic symmetry in the natural crystalline ionic lattice, supposed of structure very fine compared with the lengths of the waves. But such defect of symmetry can also be produced by mechanical deformation of a regular crystal: and the double refraction, necessarily slight, thereby introduced (in fact by bending of the lattice) even for regular crystals, must hold a clue to the intimate electric characters of the strain. An atomic lattice must be far more amenable to mechanical stress than a set of molecules could be. In amorphous aggregates, such as glass and gelatine, and even in viscous liquids under forced shearing flow, the deformation by stress of some less regular electric structure is indicated:† in fluid colloids electric ionic phenomena are of course in other ways conspicuous.‡

The magnetic achiral optical rotation of Faraday, common to all matter however regular in its crystalline form, must arise in quite different way. Here the primary phenomenon is change of free vibrational periods of the individual molecules, or perhaps atoms if the molecule is so loose a structure as is here indicated, by the extraneous magnetic field, which is the Zeeman effect: and the optical rotation is an affair of resonance due to the change of these free interacting periods,* after the manner in which ordinary dispersion is produced.†

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* The Principle of Minimal Action excludes anything more general, except chirality of the types here reviewed, *provided* the waves of radiation are long in comparison with the lattice structure.

† The recent optical study of fused quartz by Lord Rayleigh seems to open out a path in this direction.

‡ For example, the particles in a metallic suspension or (so-called) colloidal solution are now known by X-ray analysis to be crystalline; and a layer of electrons attached and locally compensating the intrinsic polarity would account for the electric charges which are the dominating feature of such suspensions. Over the whole surface this charge would be as much positive as negative, but negative electrons would be attached (in appropriate regions) by preference.

In both types of optical rotation these natural explanations concur with the forms for the equations to which the phenomena are restricted by the principle of Conservation of Energy or rather, more generally, the principle of Minimal Action.‡ Thus if we consider the case of chirally isotropic substances, the alternating electric field (P, Q, R) of the travelling radiation would introduce, through the twisting displacement of the ions, in the molecule or the lattice or both, a concomitant effective magnetisation $k\,d/dt\,(\mathrm{P}, \mathrm{Q}, \mathrm{R})$; so that its magnetic induction (a, b, c) would be given by equations of form $a = \alpha + 4\pi \mathrm{A}$ where $\mathrm{A} = k\,d\mathrm{P}/dt$.

Of the field equations of optical transmission, of type

$$\frac{\partial \mathrm{R}}{\partial y} - \frac{\partial \mathrm{Q}}{\partial z} = -\frac{da}{dt}, \qquad \frac{\partial \gamma}{\partial y} - \frac{\partial \beta}{\partial z} = 4\pi \frac{df}{dt}$$

the second could thus be written, on substitution for α, β, γ,

$$\frac{\partial c}{\partial y} - \frac{\partial b}{\partial z} = \frac{d}{dt}\left\{4\pi f + 4\pi k\left(\frac{\partial \mathrm{R}}{\partial y} - \frac{\partial \mathrm{Q}}{\partial z}\right)\right\}, \quad \text{where } f = \frac{\mathrm{K}}{4\pi \mathrm{C}^2}\,\mathrm{P},$$

agreeing in form with the equations derived from the Principle of Extremal Action.§ When K is uniform, these equations preserve both the electric and the magnetic inductions free from divergence, as they ought to be.

The general outcome is that a set of component similar lattices of electric ions prescribes in a natural manner the existence and character of the electric properties recognised in crystals: double refraction, pyro- and piezo-electricity, chiral polarisation, artificial double refraction excited by mechanical stress. It would seem even possible to infer, solely from absence of pyro-electric effect in the more symmetrical forms, that in them the crystalline lattice must be formed of ions equably spaced and not combined into molecular groups. For if the molecule were the unit, expansion by heat would alter the distance between adjacent molecules but not, or at any rate not in the same way, the distance between the two electric poles in each molecule: and it would follow by the argument indicated above, that it must alter the amount of the uncompensated surface charge, thus involving pyro-electric phenomena. The only way to avoid this conclusion would be to imagine that the positive and negative ions are so intimately blended in the molecule that it has no resultant moment, after the manner of the first crystal diagram above, until the positive and negative interlacing groups in it are displaced relatively to each other by an imposed electric field.

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* *Cf.* '*Æther and Matter*,' p. 353.

† The static magnetisation of crystals must be an affair of the orientated individual atoms, influenced only slightly by the proximity of the adjacent ones.

‡ '*Æther and Matter*,' pp. 197, 206.

§ *Loc. cit.*, § 133. The expression there given for the velocity of propagation is misprinted: *cf. infra* at the end of this paper.

Hysteresis in dielectrics, producing the residual charge of condensers, was referred by Maxwell to heterogeneity operating along with transfer of masking charges by conductance. Prompted by this ascription, Rowland found that in crystal dielectrics there was no residual charge. One can imagine dielectric fragments A, B, ... separated by a medium of different dielectric and also slight conducting quality. In a field of force, A, B, ... are polarised, but the local field is gradually diminished by conductance between A and B conveying masking charges to their surfaces. When the coatings of the condenser are discharged, the whole field throughout the dielectric is suddenly reduced, producing a sudden fall in the polarisation of A, B, ..., but not in the surface charges that masked it. The latter, now uncompensated, gradually make their way back in the reverse direction, involving accumulation of residual charge on the coatings. The actual residual charge would thus come from a small depth, but is permitted to flow back by local compensation in deeper layers. In an alternating field such as that of radiation, conductance would operate by a sort of approximation to a Grotthus chain. But in a very dilute electrolytic solution, the ionic atoms must apparently be wholly isolated from one another, whether the dielectric quality of the solvent be due to incipient atomic lattices or to orientation of polar molecules.

The internal charges in the dielectric being locally masked, the capacity of a condenser as regards sensible charge on its coatings should not be variable, as R. Kohlrausch in fact verified long ago.

The ferromagnetic hysteresis elucidated by Sir A. Ewing, and so vividly illustrated by his working models, is necessarily of different type, for there are no magnetic ions to compensate the polarisation. It requires the molecule, with its own polar magnetic moment, as unit of the structures which acquire instability under increasing extraneous force and finally fall over; yet repeated reversals do not seem to wear down completely such tendency to instabilities, which must be somehow reconstituted.

Apart from hysteresis, it has been shown long ago* that the law of Curie, paramagnetism inversely as absolute temperature, is the expression of general thermodynamic principles without involving any special theory.

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* 'Phil. Trans.,' 1897, A, p. 287.

On the same lines it has been argued* that, if electric polarisation were an affair of orientation of existing polar moments, $K-1$ should tend to vary inversely as temperature, which it seems to show no sign of doing.

The specific optical rotations of the usual active substances are of the same order of magnitude: and ideas advanced to represent their origin must be expected to throw light on that fact.

The equations expressed above lead, on elimination so that the electric force remains, to the type

$$\nabla^2 P = \frac{\partial^2}{\partial t^2}\left\{\frac{K}{c^2} P + 4\pi k\left(\frac{\partial R}{\partial y} - \frac{\partial Q}{\partial z}\right)\right\}$$

Thus for radiation travelling along z, in which therefore both the circuital vectors are on the wavefront xy,

$$\frac{\partial^2 P}{\partial z^2} = \frac{K}{c^2}\frac{\partial^2 P}{\partial t^2} - 4\pi k \frac{\partial^3 Q}{\partial z \partial t^2},$$

$$\frac{\partial^2 Q}{\partial z^2} = \frac{K}{c^2}\frac{\partial^2 Q}{\partial t^2} + 4\pi k \frac{\partial^3 P}{\partial z^2 \partial t^2},$$

so that if U represents $P + \iota Q$, $\iota = \sqrt{-1}$,

$$\frac{\partial^2 U}{\partial z^2} = \frac{\partial^2}{\partial t^2}\left(\frac{K}{c^2} + 4\pi k\iota \frac{\partial}{\partial z}\right) U,$$

indicating waves of the two circular types. If they are harmonic wave-trains involving the exponential factor

$$e^{\iota pt - \iota mz}, \qquad m = 2\pi/\lambda = p/c',$$

then
$$m^2 = \frac{p^2}{c^2}(K + 4\pi k c^2 m),$$

giving for the velocities of propagation p/m of the two circular radiations of the same period $2\pi/p$ the approximate values

$$c' = cK^{-\frac{1}{2}}(1 \pm 2\pi k K^{-\frac{1}{2}} cp).$$

The optical rotation for unit depth of the medium is the difference in π/λ or in $\frac{1}{2}p/c'$ for these two radiations, and this is $\pi p^2 k$.

Now approximating very coarsely, if there are N molecules or chiral elements per unit volume, in each of which positive and negative ions (say single charges e) are drawn asunder a distance δl_0 by the electric field and screwed through an angle θ_0, then omitting the common factor $e^{\iota pt}$

$$k\frac{\partial P}{\partial t} = \tfrac{1}{2}\iota N e r^2 \theta_0 p, \qquad \frac{K-1}{4\pi c^2} P = Ne\,\delta l_0,$$

where r represents a mean radius of transverse section of the molecule (or of a spiral filament of the lattice) so that the magnetic moment is say $\frac{1}{2}er^2\, d\theta/dt$ for each chiral unit.

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* *Loc. cit.*, p. 283.

On division N disappears and

$$\frac{\mathrm{K}-1}{4\pi c^2 k} = 2\frac{\delta l_0}{r^2\theta_0},$$

so that the optical rotation per unit depth is

$$p^2\frac{\mathrm{K}-1}{8c^2}\frac{r^2\theta_0}{\delta l_0}, \quad \text{or} \quad \frac{\pi^2}{2\lambda^2}(\mathrm{K}-1)\,r\,\frac{r\theta_0}{\delta l_0}.$$

If r is of the order of the diameter of a molecule, say 10^{-8}, this reduces to the order of $10 r\theta_0/\delta l_0$ for visible light.

Actually the optical rotation is of the order of two right angles per centimetre for quartz, and seems to range to several times less for pure active liquids. This indicates that the angle of pitch of the relative screw displacement of the positive and negative components of the structures should range around $\frac{1}{10}$, so that the chiral element may twist under an electric field about one-tenth as much as it elongates. This indication is extremely rough; but bearing in mind that powers of the velocity of radiation are involved in the estimate, one may claim that it does not detract from, but rather substantially supports, the type of picture of the phenomena which has been under review.

The Colour of the Light from the Night Sky.

By Lord Rayleigh, F.R.S.

(Received February 7, 1921.)

The general light of the sky at night is very faint, and beyond the observations of Campbell* and Slipher,† who could always detect the aurora spectrum line in temperate latitudes, nothing appears to be known of its spectroscopic or chromatic character. Slipher, indeed, suggested that the variability in its brightness recorded by Yntema might be accounted for by attributing the light mainly to a variable aurora. But this view has been controverted, rightly as I think, by Fabry.‡ My own observations, now to be recorded, indicate that at the time and place where I was working little, if any, of the light could be attributed to the green aurora line.

The great difficulty of spectroscopic observations is, of course, the want of light; though if the light were monochromatic, as, for instance, if it were all

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* 'Astr. Soc. Pacific.,' vol. 29, p. 218 (1917).

† 'Astr. Jour.,' vol. 49, p. 266 (1919).

‡ 'Astr. Jour.,' vol. 50, p. 308 (1919).